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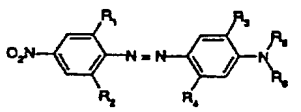
(58) Field of Search
INT CL[7] C09B 67/22

(54) Abstract Title

Dye mixtures and their use for dyeing or printing cellulose acetate-containing fibre materials

(57) This invention relates to dye mixtures, which comprise at least two dyes of formulae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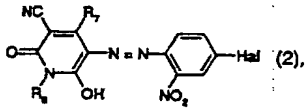
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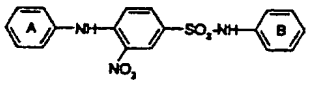
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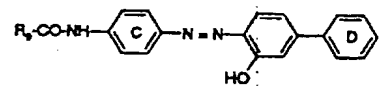
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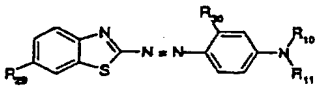
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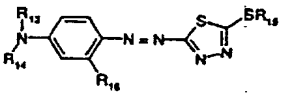
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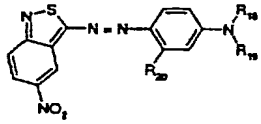
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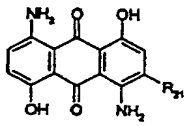
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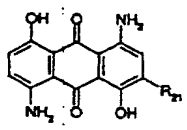
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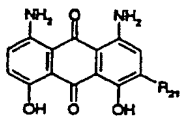
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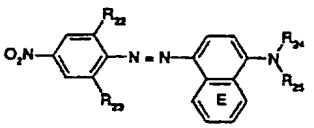
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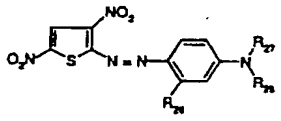
(12), wherein the variables R_1 to R_{30} are Hal, and A to E

have the meanings defined in claim 1, and to the use of these mixtures for dyeing or printing semisynthetic hydrophobic cellulose acetate-containing fibre materials. These mixtures do not stain wool or cotton if present in blends with cellulose acetate (or effect only minor staining).

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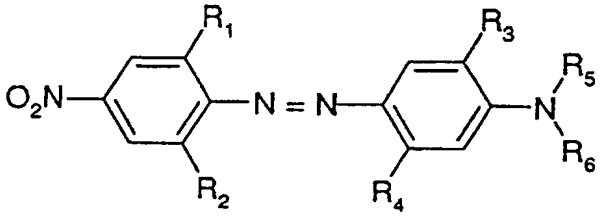
Dye mixtures and their use for dyeing or printing cellulose acetate-containing fibre materials

The present invention relates to mixtures of dyes, to their preparation and to their use for dyeing or printing cellulose acetate-containing fibre materials.

Dyes and dye mixtures for dyeing semisynthetic or synthetic hydrophobic cellulose acetate-containing fibre materials, for example cellulose-2½ acetate and cellulose triacetate, are known. However, it has been found that these dyes or the mixtures thereof do not always fully meet the highest requirements, especially with regard to reproducibility, susceptibility to the temperature of the dyebath or suitability for specific dyeing processes, in particular when a jigger or jet dyeing apparatus is used. There is thus a demand for novel dyes or dye mixtures which do not have these drawbacks.

Surprisingly, it has now been found that the mixtures of this invention substantially fulfil the above criteria.

Accordingly, this invention relates to a dye mixture, which comprises at least two dyes of formulae



(1),

wherein

R_1 is hydrogen, halogen, nitro or cyano,

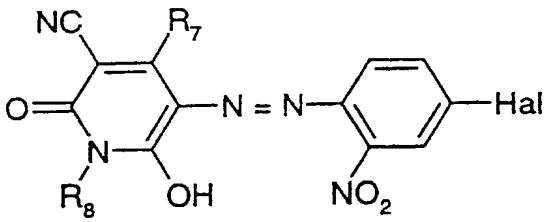
R_2 is hydrogen, halogen, nitro or cyano,

R_3 is hydrogen, halogen or C_1-C_4alkoxy,

R_4 is hydrogen, C_1-C_4alkylcarbonylamino,

R_5 is hydrogen; C_1-C_4alkyl which is unsubstituted or substituted by hydroxy, cyano, C_1-C_4-alkylcarbonyloxy,

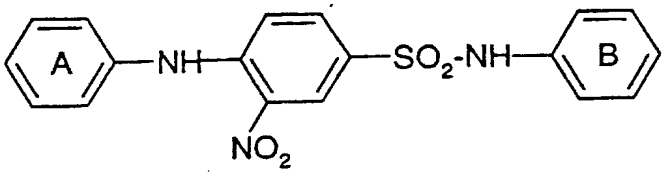
R_6 is C_1-C_4alkyl which is unsubstituted or substituted by hydroxy, cyano, C_1-C_4alkylcarbonyl-oxy, C_1-C_4alkoxycarbonyl,



(2),

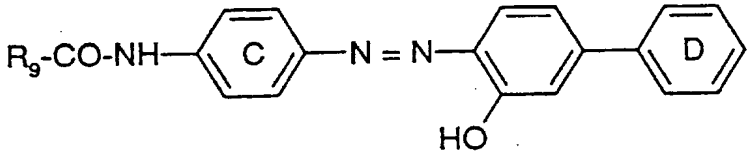
wherein

R_7 is C_1-C_4alkyl, R_8 is C_1-C_4alkyl, and Hal is halogen,



(3),

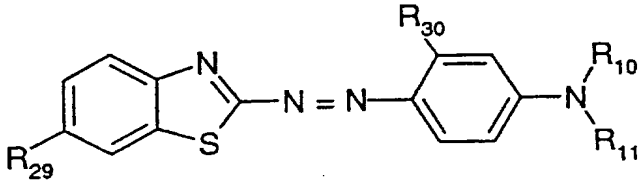
wherein the rings A and B may be further substituted,



(4),

wherein

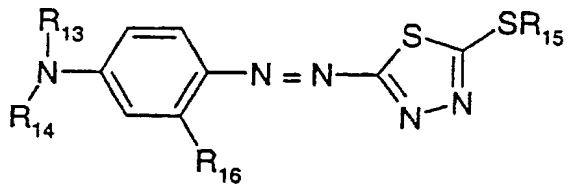
R_9 is C_1-C_4alkyl and the rings C and D may be further substituted,



(5),

wherein

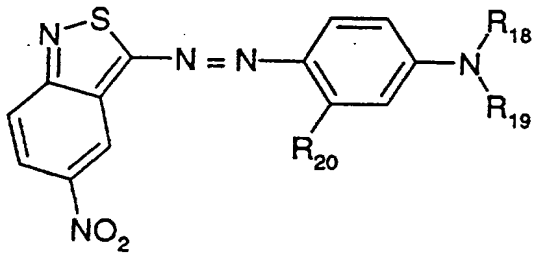
R_{10} is unsubstituted or hydroxy- or cyano-substituted C_1-C_4alkyl, R_{11} is unsubstituted or -O-COR_{12}-substituted C_1-C_4alkyl, wherein R_{12} is C_1-C_4alkyl, R_{29} is nitro, C_1-C_4alkoxy or $-SO_2CH_3$, and R_{30} is hydrogen or C_1-C_4alkyl,



(6),

wherein

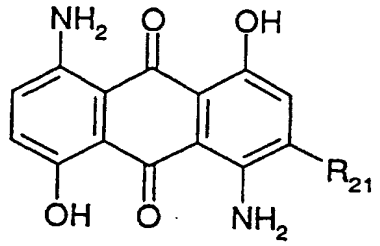
R_{13} is C_1-C_4alkyl, R_{14} is C_1-C_4alkyl, R_{15} is C_1-C_4alkyl, and R_{16} is C_1-C_4alkyl or -$NHCOR_{17}$, wherein R_{17} is C_1-C_4alkyl,



(7),

wherein

R_{18} is unsubstituted or hydroxy- or cyano-substituted C_1-C_4alkyl, R_{19} is unsubstituted or hydroxy- or C_1-C_4alkoxycarbonyl-substituted C_1-C_4alkyl, and R_{20} is hydrogen, C_1-C_4alkyl or $NHCOR_{17}$, R_{17} is C_1-C_4alkyl,



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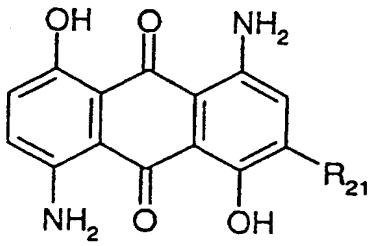

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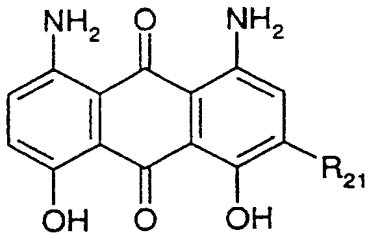
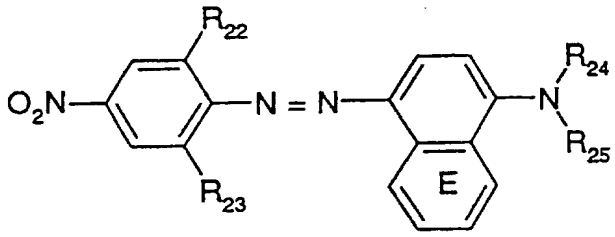


(10),

wherein R_{21} is halogen,

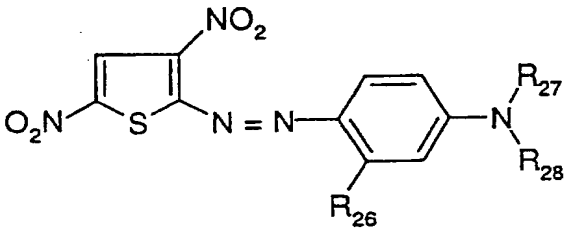


(11)

wherein

R_{22} is cyano, nitro or halogen, R_{23} is halogen, R_{24} is unsubstituted or hydroxy-substituted C_1-C_4alkyl, and R_{25} is unsubstituted or hydroxy-substituted C_1-C_4alkyl, and the naphthyl ring E may be further substituted,

and



(12),

wherein

R_{26} is C_1-C_4alkyl or the radical $NHCOR_{17}$, wherein R_{17} is C_1-C_4alkyl, R_{27} is C_1-C_4alkyl or C_1-C_4alkylcarbonyloxy-C_1-C_4alkyl, and R_{28} is C_1-C_4alkyl or C_1-C_4alkylcarbonyloxy-C_1-C_4alkyl.

The dye mixture defined above advantageously comprises at least one dye of formula (1).

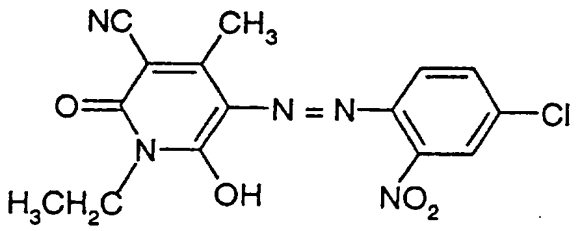
C_1-C_4Alkyl as such and as a radical in C_1-C_4alkylcarbonylamino or C_1-C_4alkylcarbonyloxy is methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl.

C_1-C_4Alkoxy as such or as a radical in C_1-C_4alkoxycarbonyl is, for example, methoxy, ethoxy propoxy or butoxy.

R_1, R_3, R_{22} and R_{23} defined as halogen are, for example, bromo or, preferably, chloro.
R_2 and R_{21} defined as halogen are, for example, chloro or, preferably, bromo.
Halogen in formula (2) is, for example, bromo or, preferably, chloro.
R_3 defined as C_1-C_4alkoxy is preferably ethoxy and, more preferably, methoxy.
R_4 defined as C_1-C_4alkylcarbonylamino is preferably propionylamino and, more preferably, acetylamino.
R_5, R_6 and R_{10} defined as C_1-C_4alkyl are propyl or isopropyl and, preferably, ethyl.
R_7, R_9,R_{12}, R_{16}, R_{17}, R_{20}, R_{26} and R_{30} defined as C_1-C_4alkyl are preferably ethyl and, more preferably, methyl.
R_8, R_{11}, R_{15}, R_{18}, R_{19}, R_{27} and R_{28} defined as C_1-C_4alkyl are preferably methyl and, more preferably, ethyl.
R_{13}, R_{14}, R_{24} and R_{25} defined as C_1-C_4alkyl are preferably ethyl and, more preferably, propyl.
R_{27} and R_{28} are preferably C_1-C_4alkyl.
R_{29} is preferably nitro or the radical $-SO_2CH_3$.

The C_1-C_4alkyl radicals are usually substituted once or twice with the substituents cited above.

Preferred dye mixtures are those, which comprise at least two dyes of formulae



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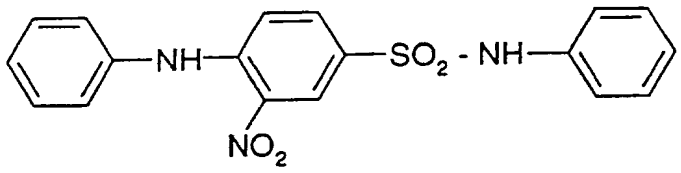

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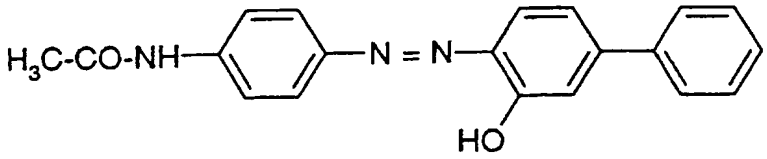

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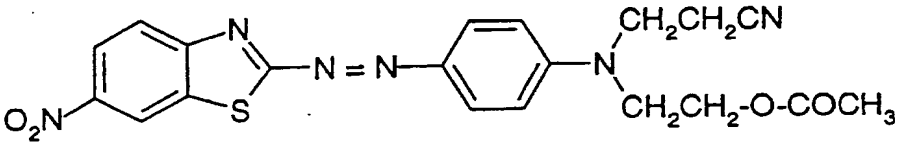

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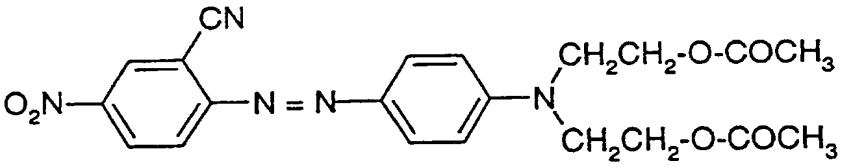

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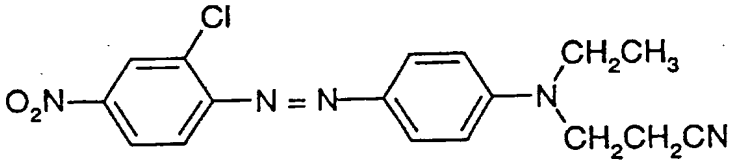

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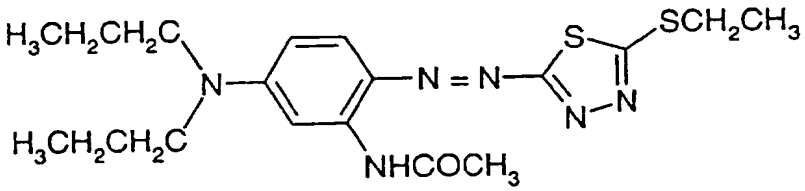

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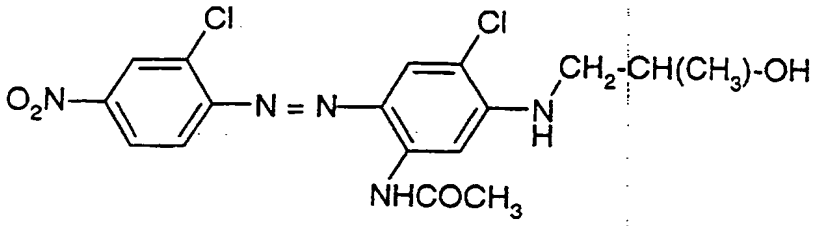

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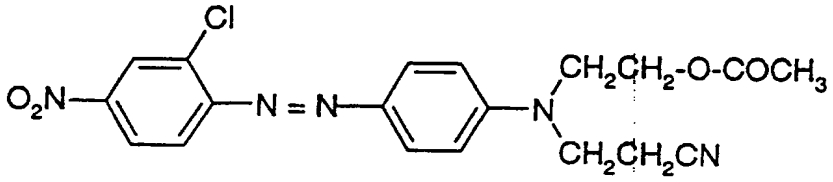

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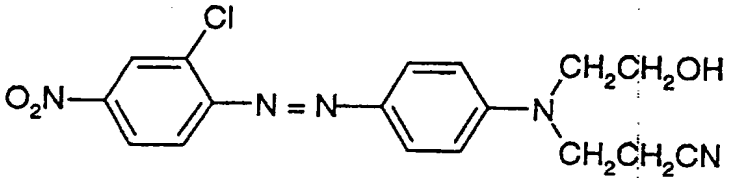

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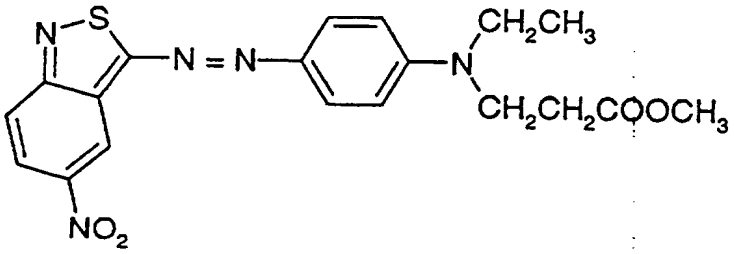

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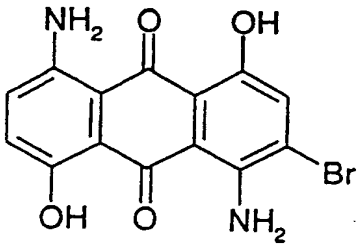

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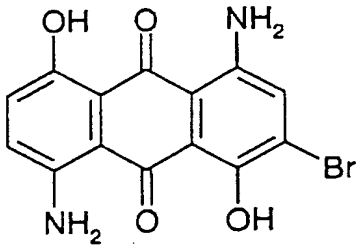

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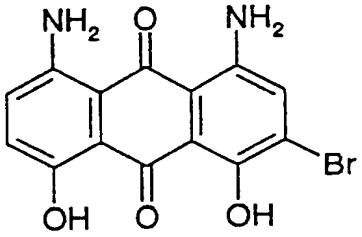

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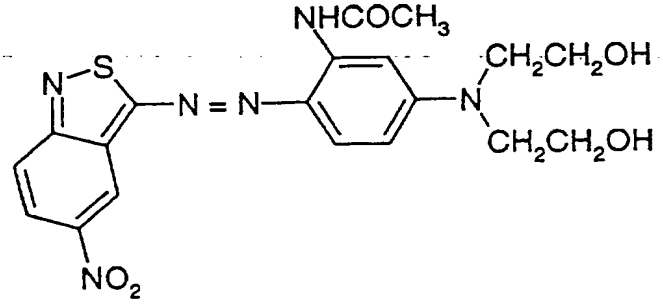

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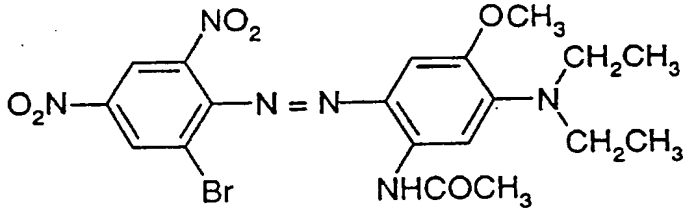

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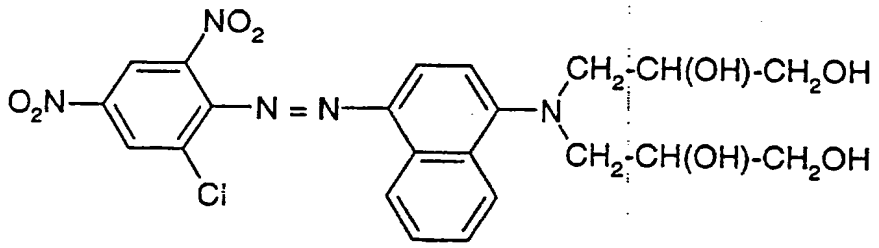

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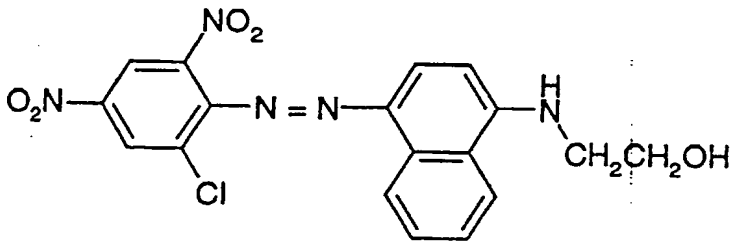

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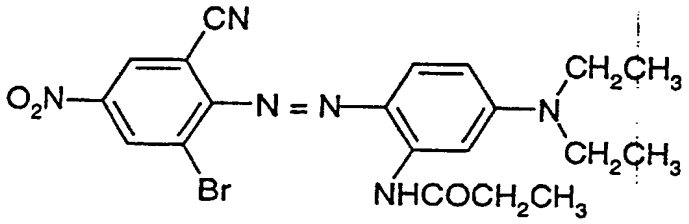

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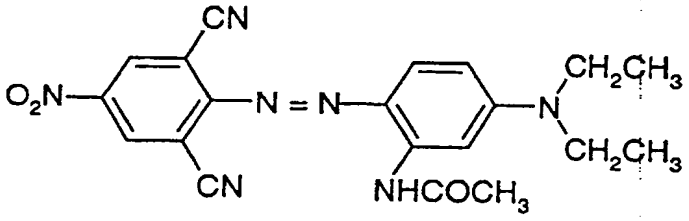

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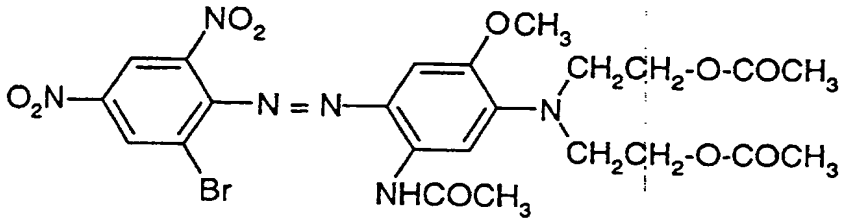

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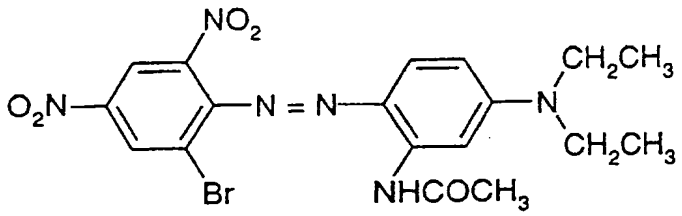

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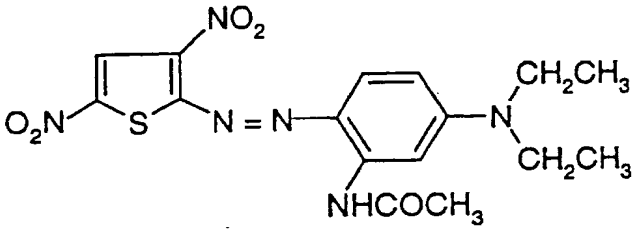

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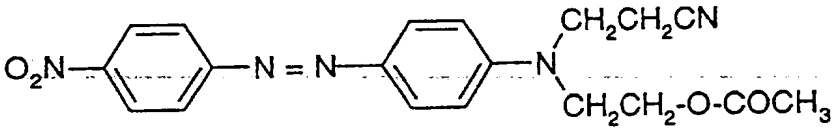

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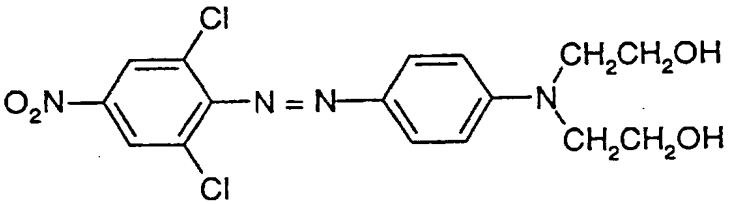

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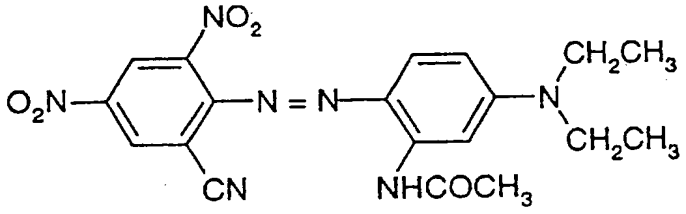

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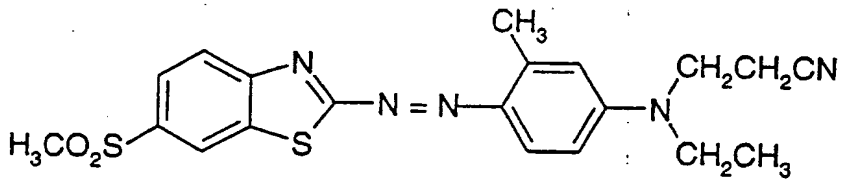

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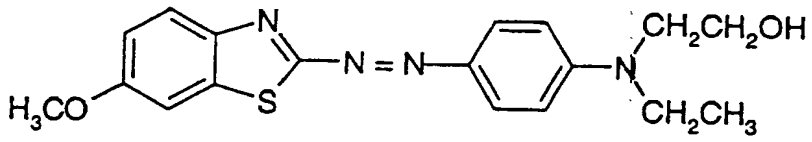

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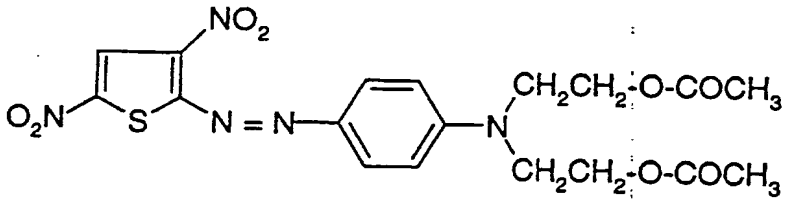


(41).

The dyes of formulae (1) to (41) are known or can be prepared by commonly known methods.

A particularly preferred dye mixture is that, which comprises the dyes of formulae (23) and (41).

A particularly preferred dye mixture is that, which comprises the dyes of formulae (13), (14) and (15).

Another particularly preferred dye mixture is that, which comprises the dyes of formulae (17), (18), (21) and (22).

A particularly preferred dye mixture is also that, which comprises the dyes of formulae (16), (17), (39) and (18).

A particularly preferred dye mixture is also that, which comprises the dyes of formulae (20), (19) and (39).

Also particularly preferred is a dye mixture, which comprises the dyes of formulae (23), (24), (25) and (26).

Another particularly preferred dye mixture is that, which comprises the dyes of formulae (32), (38), (23), (28), (33) and (27).

Also particularly preferred is a dye mixture, which comprises the dyes of formulae (29), (30), (23), (32), (28), (34) and (33).

Another particularly preferred dye mixture is that, which comprises the dyes of formulae (35), (27) and (28).

A particularly preferred dye mixture is also that, which comprises the dyes of formulae (29), (30), (28), (36), (32), (34), (33), (38) and (17).

Another particularly preferred dye mixture is that, which comprises the dyes of formulae (24), (25), (26), (30), (29), (23), (37), (13), (34) and (33).

Also particularly preferred is a dye mixture, which comprises the dyes of formulae (28), (30), (29), (13), (21), (22), (34), (33), (36), (32) and (38).

A particularly preferred dye mixture is also that, which comprises the dyes of formulae (16), (17), (18) and (40).

Another particularly preferred dye mixture is that, which comprises the dyes of formulae (19), (20) and (40).

A very particularly preferred dye mixture is that, which comprises
5 to 15 parts by weight of the dye of formula (13),
22 to 48 parts by weight of the dye of formula (14), and
12 to 37 parts by weight of the dye of formula (15).

Another very particularly preferred dye mixture is that, which comprises
12 to 39 parts by weight of the dye of formula (18),
5 to 18 parts by weight of the dye of formula (17),
15 to 36 parts by weight of the dye of formula (21), and
2 to 7 parts by weight of the dye of formula (22).

Also very particularly preferred is a dye mixture, which comprises
6 to 23 parts by weight of the dye of formula (18),
7 to 23 parts by weight of the dye of formula (17),
10 to 31 parts by weight of the dye of formula (39), and
6 to 23 parts by weight of the dye of formula (16).

Another very particularly preferred dye mixture is that, which comprises
7 to 22 parts by weight of the dye of formula (20),
12 to 44 parts by weight of the dye of formula (19), and
10 to 34 parts by weight of the dye of formula (39).

Likewise very particularly preferred is a dye mixture, which comprises
9 to 24 parts by weight of the dye of formula (24),
9 to 24 parts by weight of the dye of formula (25),
9 to 24 parts by weight of the dye of formula (26), and
10 to 28 parts by weight of the dye of formula (23).

Also very particularly preferred is a dye mixture, which comprises
4 to 19 parts by weight of the dye of formula (32),
5 to 19 parts by weight of the dye of formula (38),
6 to 21 parts by weight of the dye of formula (23),
3 to 15 parts by weight of the dye of formula (33),
3 to 15 parts by weight of the dye of formula (28), and
5 to 21 parts by weight of the dye of formula (27).

Another very particularly preferred dye mixture is that, which comprises
7 to 25 parts by weight of the dye of formula (29),
8 to 25 parts by weight of the dye of formula (30),
3 to 14 parts by weight of the dye of formula (23),
2 to 12 parts by weight of the dye of formula (32),
1 to 8 parts by weight of the dye of formula (28),
2 to 10 parts by weight of the dye of formula (34), and
1 to 6 parts by weight of the dye of formula (33).

Also very particularly preferred is a dye mixture, which comprises
15 to 54 parts by weight of the dye of formula (35),
10 to 35 parts by weight of the dye of formula (27), and
2 to 11 parts by weight of the dye of formula (28).

Likewise very particularly preferred is a dye mixture, which comprises
8 to 25 parts by weight of the dye of formula (29),
3 to 11 parts by weight of the dye of formula (30),
1 to 8 parts by weight of the dye of formula (28),
3 to 6 parts by weight of the dye of formula (36),
3 to 12 parts by weight of the dye of formula (32),
2 to 9 parts by weight of the dye of formula (34),
3 to 13 parts by weight of the dye of formula (33),
0.5 to 3 parts by weight of the dye of formula (17), and
4 to 13 parts by weight of the dye of formula (38).

Also very particularly preferred is a dye mixture, which comprises
1.2 to 6 parts by weight of the dye of formula (24),
1.2 to 6 parts by weight of the dye of formula (25),
1.2 to 6 parts by weight of the dye of formula (26),
3 to 13 parts by weight of the dye of formula (30),
4 to 17 parts by weight of the dye of formula (29),
1 to 7 parts by weight of the dye of formula (23),
6 to 19 parts by weight of the dye of formula (37),
4 to 14 parts by weight of the dye of formula (13),
1 to 5 parts by weight of the dye of formula (34), and
1 to 7 parts by weight of the dye of formula (33).

Another very particularly preferred dye mixture is that, which comprises
2 to 9 parts by weight of the dye of formula (28),
2 to 10 parts by weight of the dye of formula (30),
3 to 13 parts by weight of the dye of formula (29),
2 to 9 parts by weight of the dye of formula (13),
2 to 10 parts by weight of the dye of formula (21),

0.3 to 3 parts by weight of the dye of formula (22)
1 to 6 parts by weight of the dye of formula (34),
1 to 7 parts by weight of the dye of formula (33),
2 to 11 parts by weight of the dye of formula (36),
2 to 11 parts by weight of the dye of formula (32), and
2 to 11 parts by weight of the dye of formula (38).

The novel dye mixtures can be used as dyes for dyeing and printing semisynthetic hydrophobic, cellulose acetate-containing fibre materials, in particular textile materials. Textile materials consisting of blended fabrics containing semisynthetic hydrophobic, cellulose acetate-containing textile materials and e.g. viscose or polyamide can also be dyed or printed by means of the dye mixtures of this invention.

Suitable semisynthetic hydrophobic, cellulose acetate-containing textile materials are especially cellulose-2$^1/_2$acetate and cellulose triacetate.

The novel compounds are applied to the textile materials by known dyeing processes. Cellulose-2$^1/_2$acetate, for example, is preferably dyed in the temperature range from about 65 to 95°C and cellulose triacetate in the temperature range from 65 to 130°C, preferably from 90 to 125°C.

The novel dye mixtures do not stain wool and cotton simultaneously present in the dyebath or effect only minor staining (very good resist), so that they can also readily be used for dyeing cellulose acetate/wool and cellulose acetate/cellulose blends.

The novel dye mixtures are suitable for dyeing by the thermosol, pad steam, pad roll and pad jig process and for printing processes.

The cited textile material can be in a very wide range of forms of presentation, such as fibre, thread or nonwoven fabric, or wovens or knitgoods.

It is expedient to convert the novel dye mixtures, before use, into a dye formulation. This is done by milling the dye mixture to an average particle size of 0.1 to 10 microns. Milling can usefully be carried out in the presence of dispersants. Typically, the dried dye mixture is

milled with one or more than one dispersant, or kneaded in paste form with one or more than one dispersant, and thereafter dried under vacuum or by spray drying. Printing pastes and dyebaths can be prepared by adding water to the formulations so obtained. Suitable dispersants are those customarily used for dyeing with disperse dyes, for example the dispersants cited in EP-A-0 280 654.

However, the dyes can also be formulated singly, as described above, and then converted into the corresponding dye formulation by a simple blending process.

The amount of the dispersant(s) present in the dye formulation can range from 0 to 75 % by weight, based on the weight of the dye formulation.

The amount of the dye mixtures in the dye liquor depends on the desired shade. Amounts which have been found to be useful range from 0.01 to 15 % by weight, preferably from 0.02 to 10 % by weight, most preferably from 0.1 to 5 % by weight, based on the weight of the fibre material to be dyed.

The dye liquors can also contain other additives, for example dyeing auxiliaries, wetting agents and defoamers.

The dye liquors can also contain mineral acids, for example sulfuric acid or phosphoric acid, or, preferably, organic acids, for example fumaric acid or acetic acid and/or salts, such as ammonium acetate or sodium sulfates. The acids serve mainly to adjust the pH value of the dye liquors which is preferably from 4 to 7.

The customary thickeners will be used for printing, for example modified or nonmodified natural products, such as alginates, British gum, gum arabic, crystal gum, carob bean gum, tragacanth, carboxymethylcellulose, hydroxyethylcellulose, starch or synthetic products, for example polyacrylamides, polyacrylic acid or copolymers thereof, or polyvinyl alcohols.

The cited materials, especially the cellulose-$2^1/_2$acetate and cellulose triacetate, are dyed with the novel dye mixtures in level shades having very good end use properties, in particular good fastness to light, thermofixation, pleating, chlorinating and good fastness to wet treatments, such as fastness to water, sweat and washing; and the dyeings are also distin-

guished by excellent fastness to rubbing. To be highlighted in particular is the good dye yield and good build-up of the novel dye mixtures.

The novel dye mixtures can also be readily used for obtaining mixed shades in conjunction with other dyes.

In addition, the novel dye mixtures are also very suitable for dyeing hydrophobic textile material from supercritical CO_2.

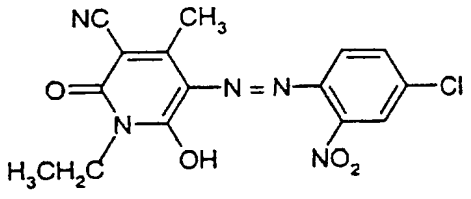
Further objects of the invention are the aforementioned use of the dye mixtures of this invention and a process for dyeing or printing semisynthetic hydrophobic, cellulose acetate-containing fibre material, in particular textile material consisting of cellulose-$2^1/_2$acetate and cellulose triacetate, which comprises applying the novel dye mixture to said material or incorporating it therein. Other substrates which can be treated by the process of this invention and preferred process conditions have been discussed above in the more detailed description of the use of the novel dye mixtures. The definitions and preferred meanings mentioned for the dyes and dye mixtures apply to the dye mixtures used according to this invention.

This invention also relates to the semisynthetic, cellulose acetate-containing hydrophobic fibre material, preferably to textile material consisting of cellulose-$2^1/_2$acetate and cellulose triacetate, which is dyed or printed by the cited process.

This invention is illustrated in more detail by the following Examples. Parts and percentages are by weight, unless otherwise stated. Temperatures are given in degrees Celsius. The relationship between parts by weight and parts by volume is the same as that of the gramme and the cubic centimetre.

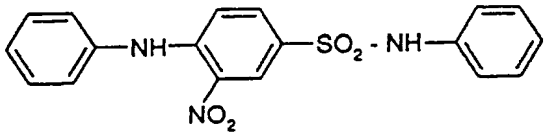
Example 1:

In an AHIBA laboratory dyeing apparatus, a 10 g piece of a textile material consisting of cellulose-$2^1/_2$acetate is dipped at 40°C into a liquor containing
0.5 g/l of a commercially available penetration accelerator (®Cibaflow CIR),
0.3 g/l of a commercially available dispersant (®Albatex PON conc.), and
0.2 g of a dye formulation (A) containing
0.0122 g of the dye of formula



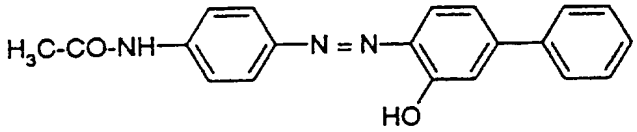
(13),

0.0484 g of the dye of formula



(14),

0.031 g of the dye of formula



(15) and

0.1084 g of a commercially available dispersant (®Dispergator CC), which is adjusted to pH 6.0 with 80% fumaric acid. The liquor is then heated to 90°C at a heating rate of 1-2° C/minute and the textile material is dyed at this temperature for 60 minutes.

The liquor is then cooled to 40° C and the dyed textile material is washed with warm and cold water and then dried.

This gives a brilliant golden yellow dyeing having excellent end use fastness properties.

Examples 2 to 10:

The procedure of Example 1 is repeated, but replacing the 0.2 g of the dye formulation (A) used in that Example with the dye formulations (B) to (K) listed in Table 1 in the amounts stated there, which also yields dyeings having very good end use fastness properties.

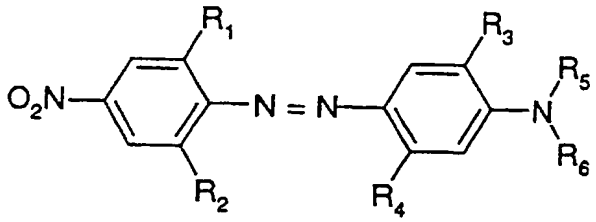
Table 1:

Dye formulation	Composition of the dye formulation	Amount	Shade
(B)	14.0 % by weight of the dye of formula (18), 6.9 % by weight of the dye of formula (17), 16.83 % by weight of the dye of formula (21), 2.97 % by weight of the dye of formula (22), and 59.3 % by weight of a commercially available dispersant	0.1 g	scarlet
(C)	8.0 % by weight of the dye of formula (18), 9.2 % by weight of the dye of formula (17), 12.0 % by weight of the dye of formula (39), 8.0 % by weight of the dye of formula (16), and 62.8 % by weight of a commercially available dispersant	0.1 g	red
(D)	8.3 % by weight of the dye of formula (20), 15.2 % by weight of the dye of formula (19), 12.0 % by weight of the dye of formula (39), and 64.5 % by weight of a commercially available dispersant	0.1 g	pink
(E)	9.93 % by weight of the dye of formula (24), 9.93 % by weight of the dye of formula (25), 9.93 % by weight of the dye of formula (26), 11.8 % by weight of the dye of formula (23), and 58.41 % by weight of a commercially available dispersant	0.17 g	blue
(F)	5.9 % by weight of the dye of formula (32), 6.5 % by weight of the dye of formula (38), 7.1 % by weight of the dye of formula (23), 4.2 % by weight of the dye of formula (28), 4.5 % by weight of the dye of formula (33), 6.3 % by weight of the dye of formula (27), and 65.5 % by weight of a commercially available dispersant	0.18 g	blue
(G)	9.0 % by weight of the dye of formula (29), 9.6 % by weight of the dye of formula (30), 4.7 % by weight of the dye of formula (23), 3.6 % by weight of the dye of formula (32), 1.8 % by weight of the dye of formula (28), 2.9 % by weight of the dye of formula (34), 1.7 % by weight of the dye of formula (33), and 66.7 % by weight of a commercially available dispersant	0.45 g	dark blue

(H)	17.7 % by weight of the dye of formula (35), 12.6 % by weight of the dye of formula (27), 3.2 % by weight of the dye of formula (28), and 66.5 % by weight of a commercially available dispersant	0.15 g	turquoise
(I)	9.1 % by weight of the dye of formula (29), 4.2 % by weight of the dye of formula (30), 3.2 % by weight of the dye of formula (28), 2.3 % by weight of the dye of formula (36), 4.5 % by weight of the dye of formula (32), 3.8 % by weight of the dye of formula (34), 4.5 % by weight of the dye of formula (33), 5.0 % by weight of the dye of formula (38), 0.7 % by weight of the dye of formula (17), and 62.7 % by weight of a commercially available dispersant	0.45 g	navy
(J)	1.4 % by weight of the dye of formula (24), 1.4 % by weight of the dye of formula (25), 1.4 % by weight of the dye of formula (26), 4.6 % by weight of the dye of formula (30), 6.0 % by weight of the dye of formula (29), 1.8 % by weight of the dye of formula (23), 7.4 % by weight of the dye of formula (37), 5.1 % by weight of the dye of formula (13), 1.5 % by weight of the dye of formula (34), 1.7 % by weight of the dye of formula (33), and 67.7 % by weight of a commercially available dispersant	0.45 g	black
(K)	2.7 % by weight of the dye of formula (28), 3.2 % by weight of the dye of formula (30), 4.1 % by weight of the dye of formula (29), 3.0 % by weight of the dye of formula (13), 2.72 % by weight of the dye of formula (21), 0.48 % by weight of the dye of formula (22), 1.5 % by weight of the dye of formula (34), 1.6 % by weight of the dye of formula (33), 3.5 % by weight of the dye of formula (36), 3.4 % by weight of the dye of formula (32), 3.7 % by weight of the dye of formula (38), and 70.1 % by weight of a commercially available dispersant	0.5 g	black

What is claimed is

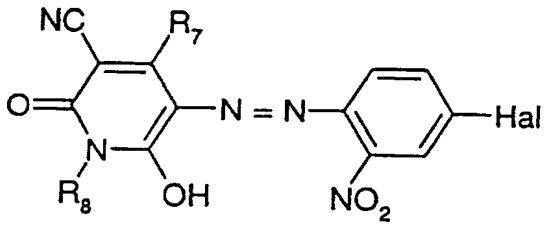
1. A dye mixture, which comprises at least two dyes of formula



(1),

wherein

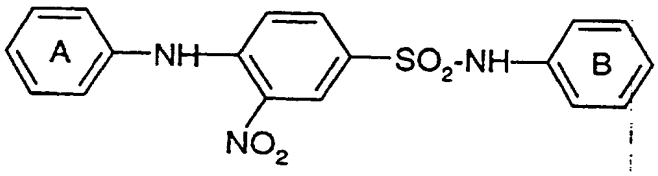
R_1 is hydrogen, halogen, nitro or cyano, R_2 is hydrogen, halogen, nitro or cyano, R_3 is hydrogen, halogen or C_1-C_4alkoxy, R_4 is hydrogen, C_1-C_4alkylcarbonylamino, R_5 is hydrogen; C_1-C_4alkyl which is unsubstituted or substituted by hydroxy, cyano, C_1-C_4alkylcarbonyloxy, R_6 is C_1-C_4alkyl which is unsubstituted or substituted by hydroxy, cyano, C_1-C_4alkylcarbonyloxy, C_1-C_4alkoxycarbonyl,



(2),

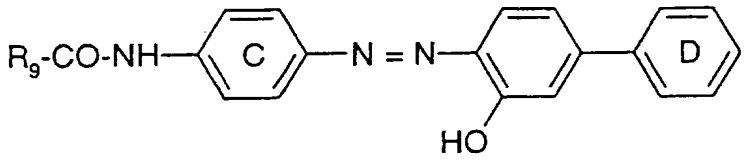
wherein

R_7 is C_1-C_4alkyl, R_8 is C_1-C_4alkyl, and Hal is halogen,



(3),

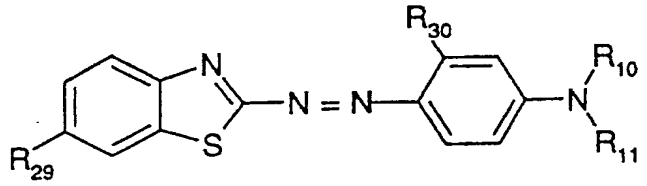
wherein the rings A and B may be further substituted,



(4),

wherein

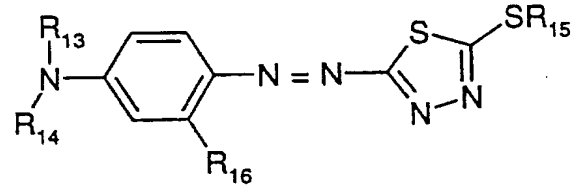
R_9 is C_1-C_4alkyl and the rings C and D may be further substituted,



(5),

wherein

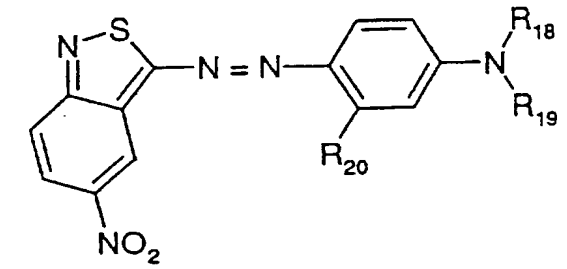
R_{10} is unsubstituted or hydroxy- or cyano-substituted C_1-C_4alkyl, R_{11} is unsubstituted or -O-COR_{12}-substituted C_1-C_4alkyl, wherein R_{12} is C_1-C_4alkyl, R_{29} is nitro, C_1-C_4alkoxy or $-SO_2CH_3$, and R_{30} is hydrogen or C_1-C_4alkyl,



(6),

wherein

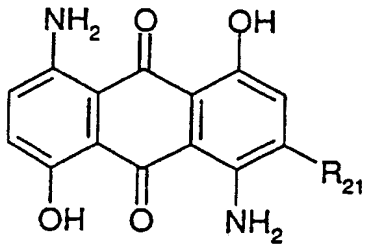
R_{13} is C_1-C_4alkyl, R_{14} is C_1-C_4alkyl, R_{15} is C_1-C_4alkyl, and R_{16} is C_1-C_4alkyl or -NHCOR_{17}, wherein R_{17} is C_1-C_4alkyl,



(7),

wherein

R_{18} is unsubstituted or hydroxy- or cyano-substituted C_1-C_4alkyl, R_{19} is unsubstituted or hydroxy- or C_1-C_4alkoxycarbonyl-substituted C_1-C_4alkyl, and R_{20} is hydrogen, C_1-C_4alkyl or $NHCOR_{17}$, R_{17} is C_1-C_4alkyl,



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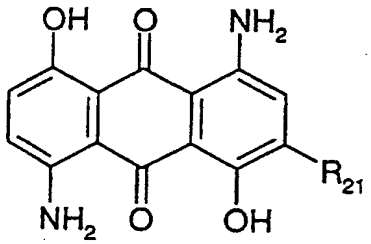
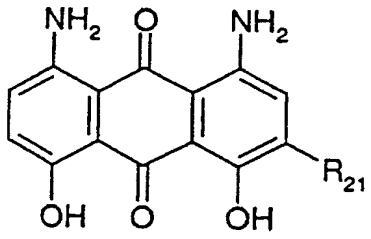
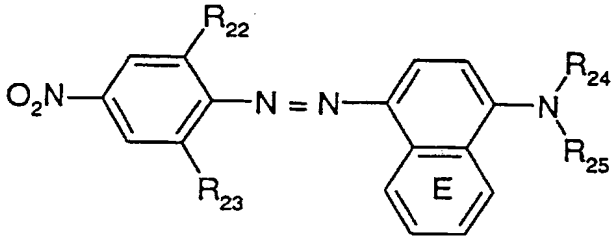


(9),



(10),

wherein R_{21} is halogen,

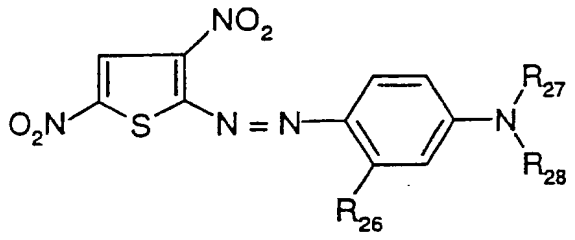


(11)

wherein

R_{22} is cyano, nitro or halogen, R_{23} is halogen, R_{24} is unsubstituted or hydroxy-substituted C_1-C_4alkyl, and R_{25} is unsubstituted or hydroxy-substituted C_1-C_4alkyl, and the naphthyl ring E may be further substituted,

and



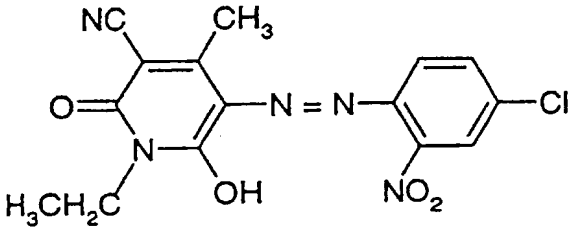
(12),

wherein

R_{26} is C_1-C_4alkyl or the radical $NHCOR_{17}$, wherein R_{17} is C_1-C_4alkyl, R_{27} is C_1-C_4alkyl or C_1-C_4alkylcarbonyloxy-C_1-C_4alkyl, and R_{28} is C_1-C_4alkyl or C_1-C_4alkylcarbonyloxy-C_1-C_4alkyl.

2. A dye mixture according to claim 1, wherein in formula (12) R_{27} is C_1-C_4alkyl and R_{28} is C_1-C_4alkyl, and in formula (5) R_{29} is nitro or the radical $-SO_2CH_3$.

3. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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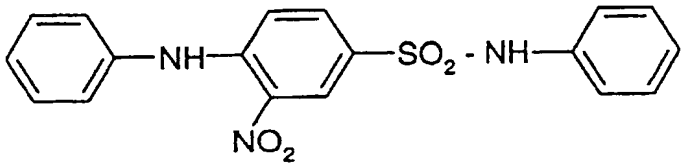

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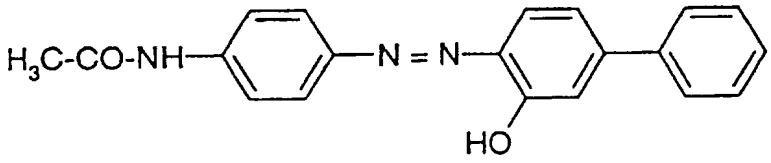
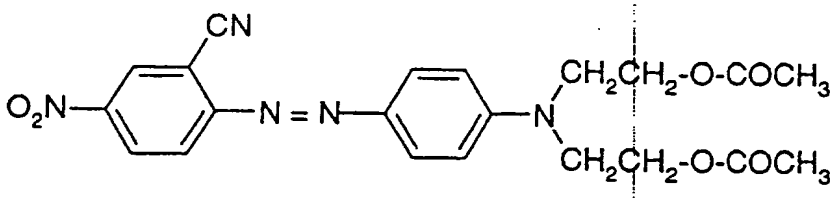


(15).

4. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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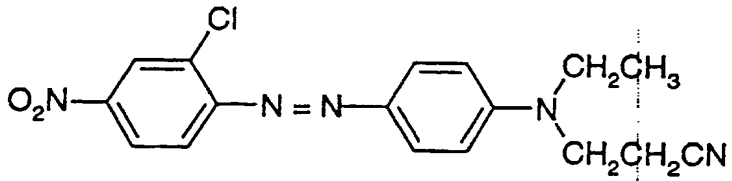

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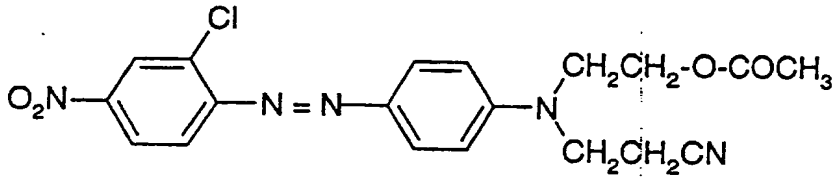

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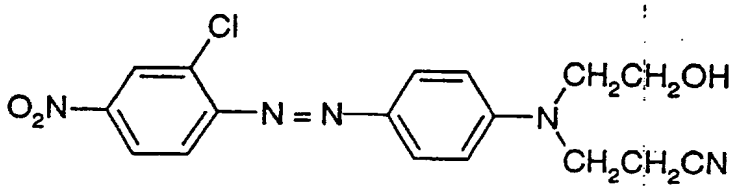
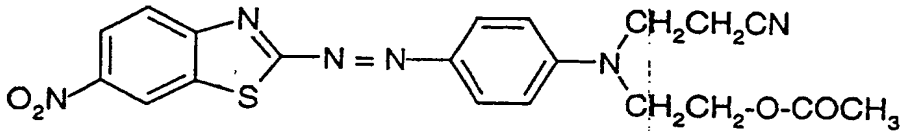


(22).

5. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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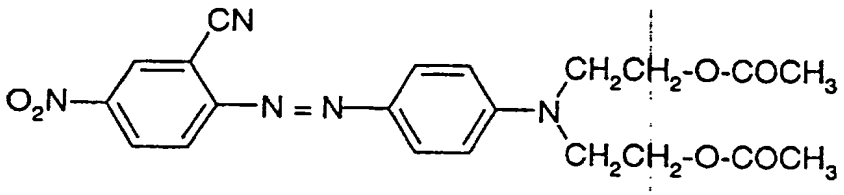

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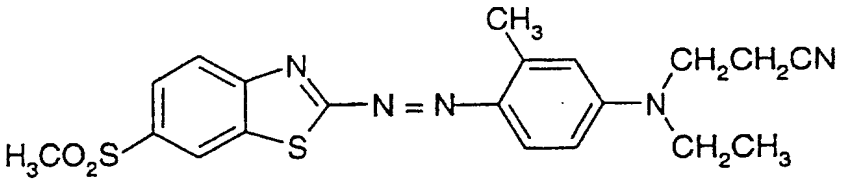

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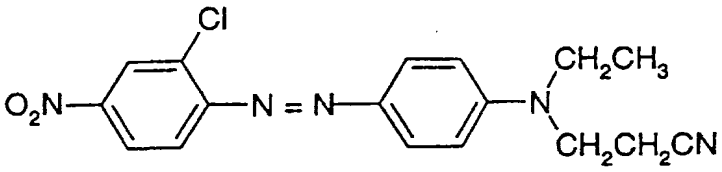
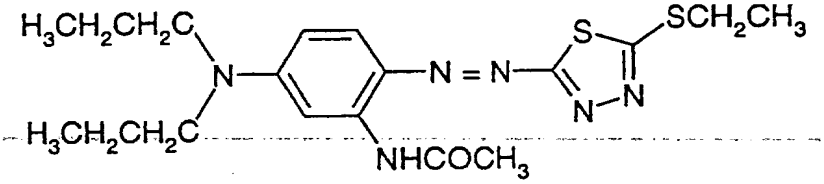


(18).

6. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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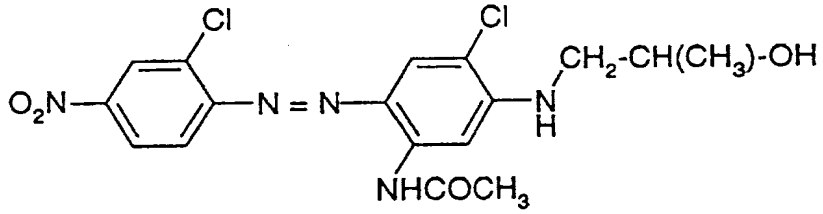

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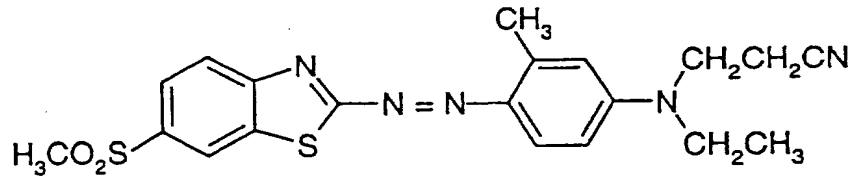
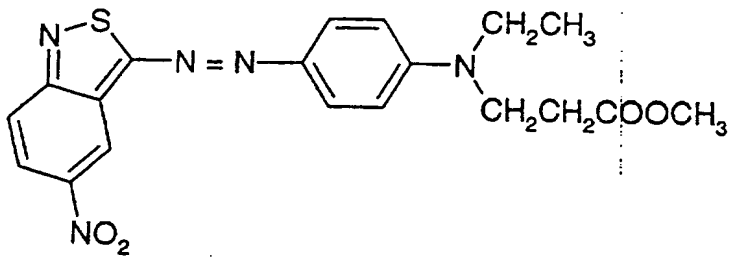


(39).

7. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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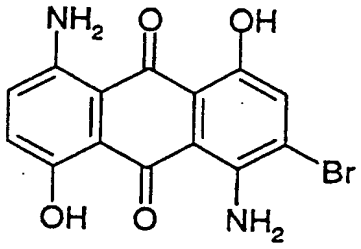

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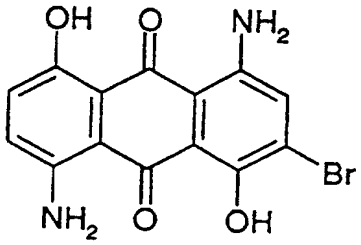

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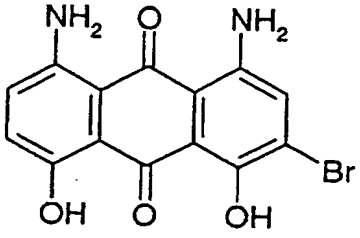
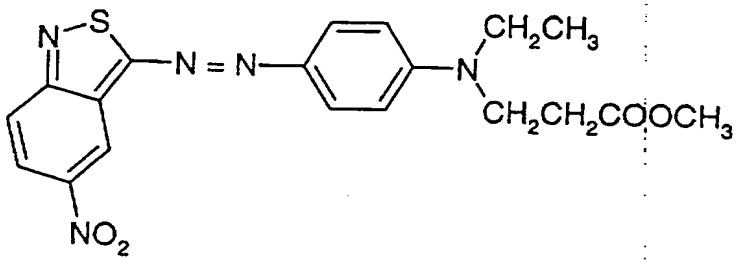


(26).

8. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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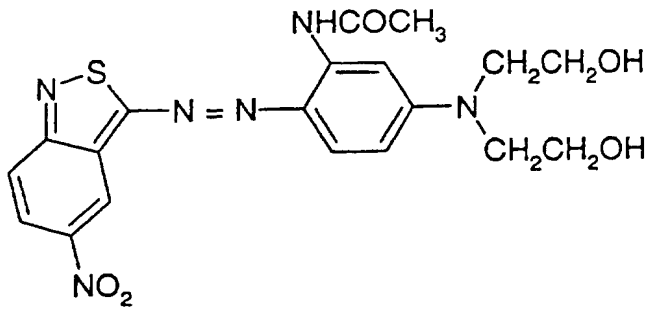

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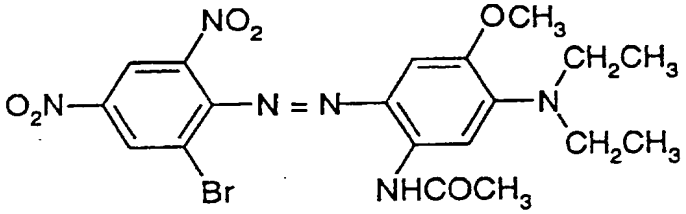

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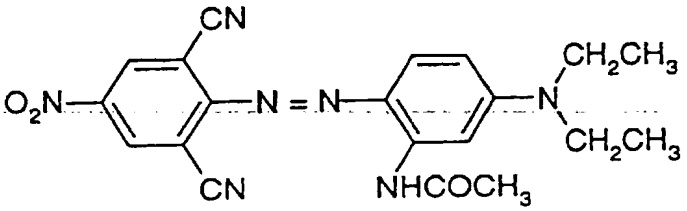

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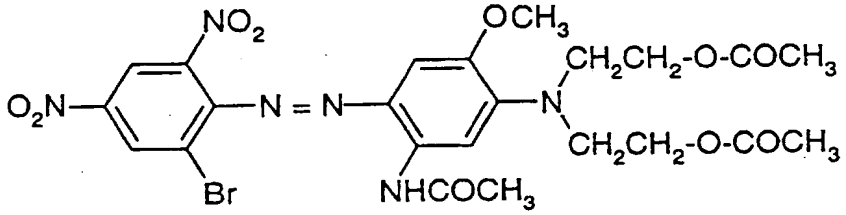

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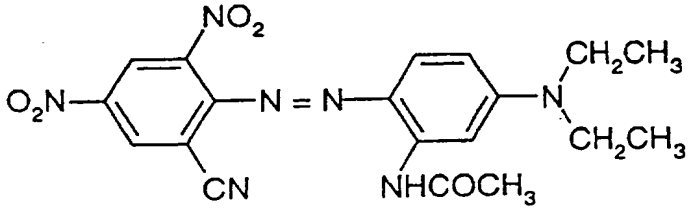
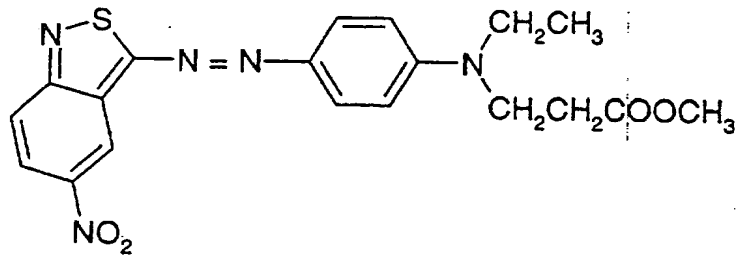


(38).

9. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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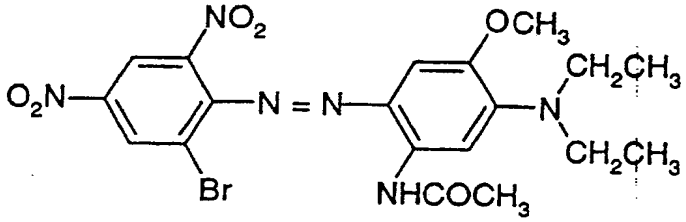

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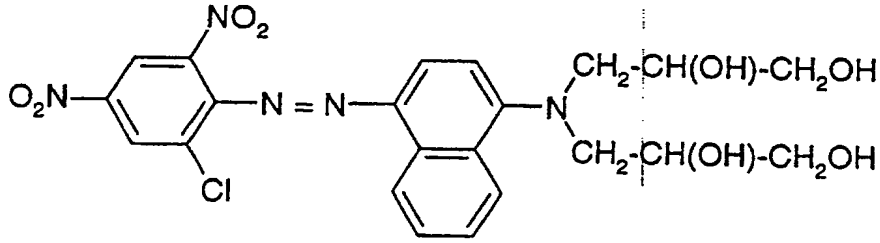

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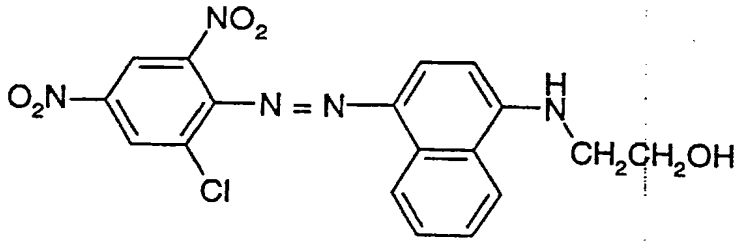

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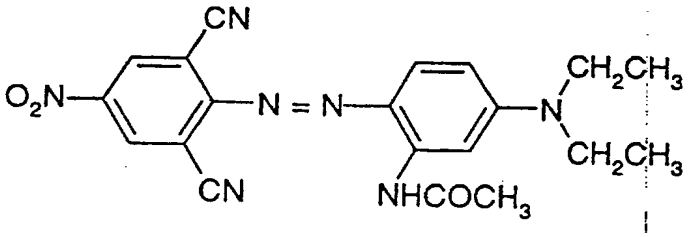

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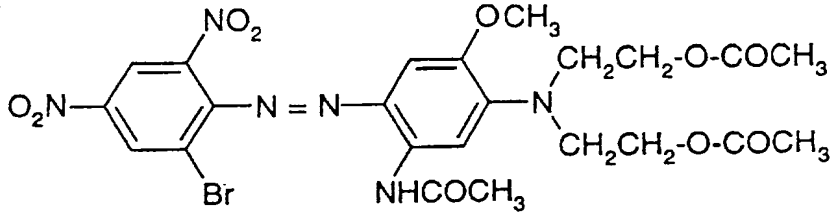

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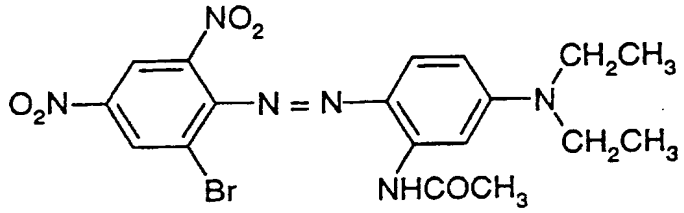
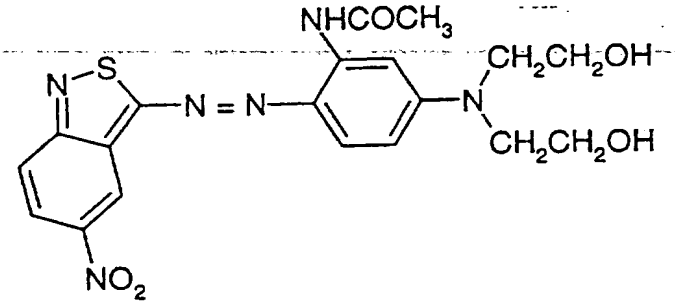


(34).

10. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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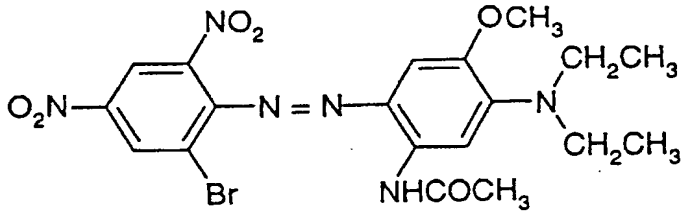

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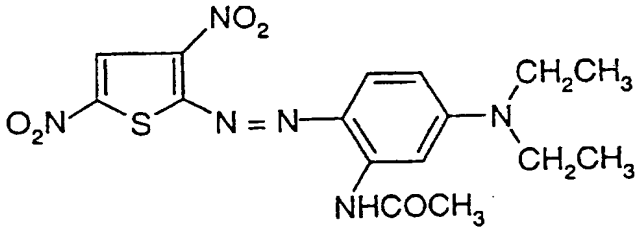
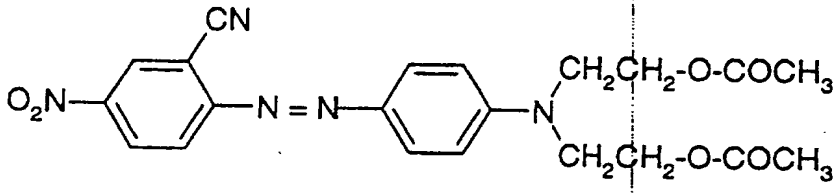


(35).

11. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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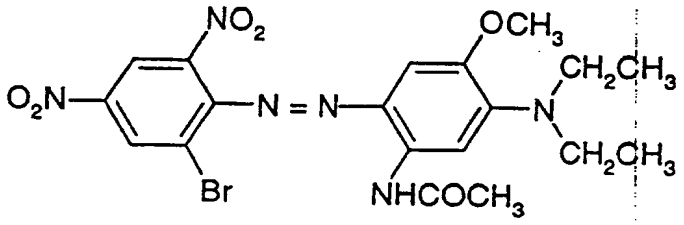

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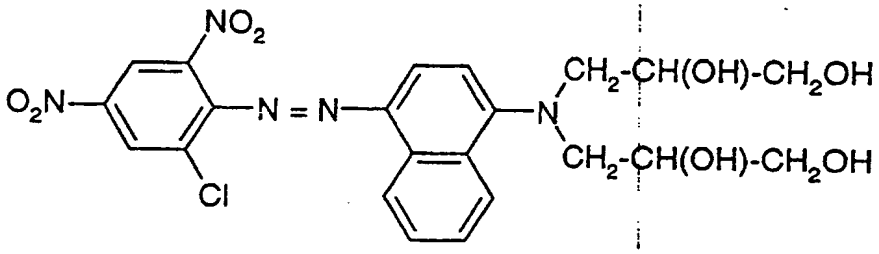

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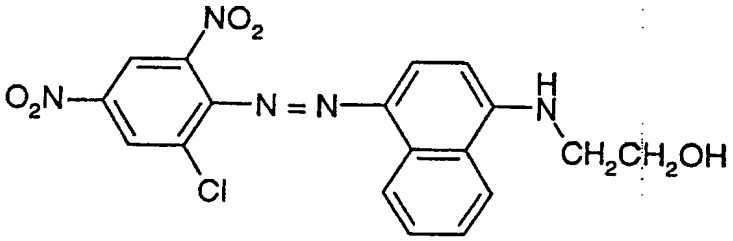

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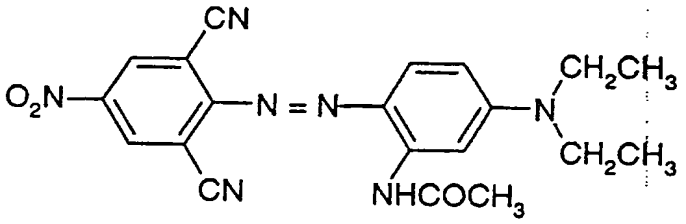

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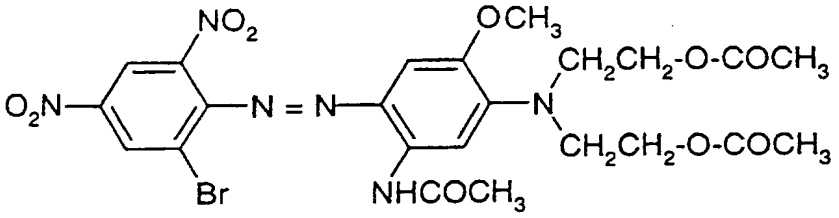

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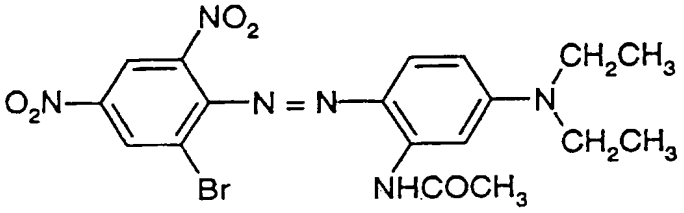

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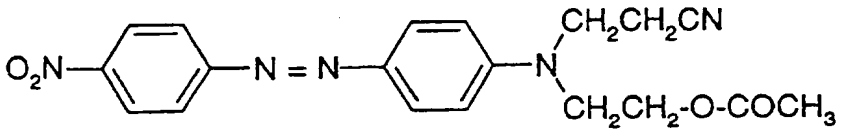

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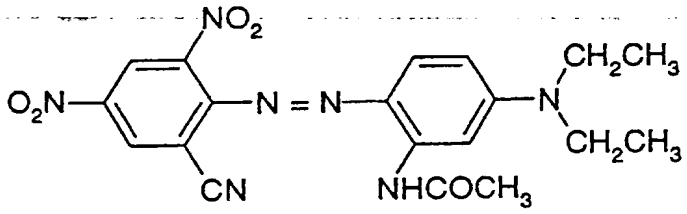
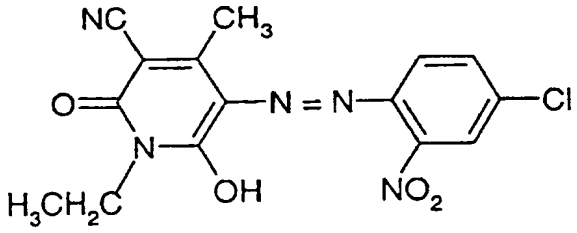


(38).

12. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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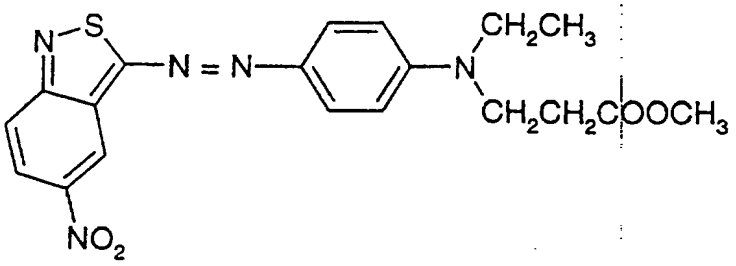

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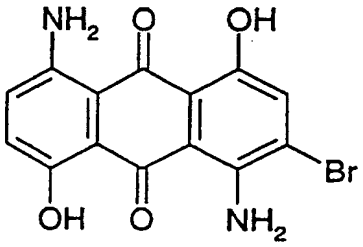

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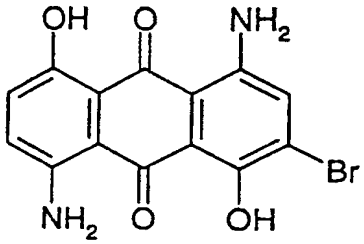

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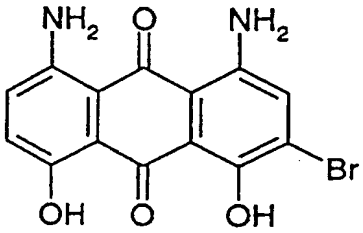

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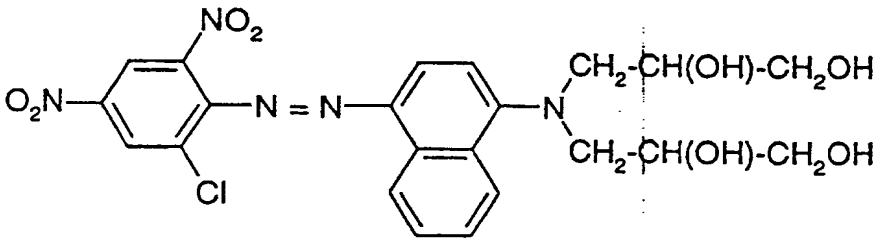

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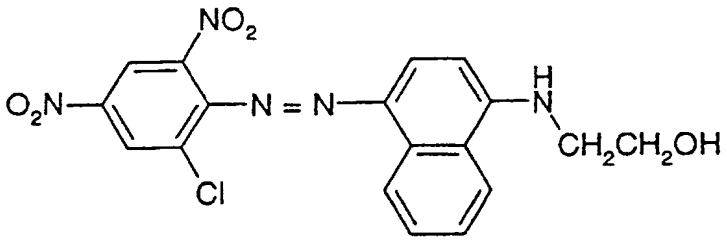

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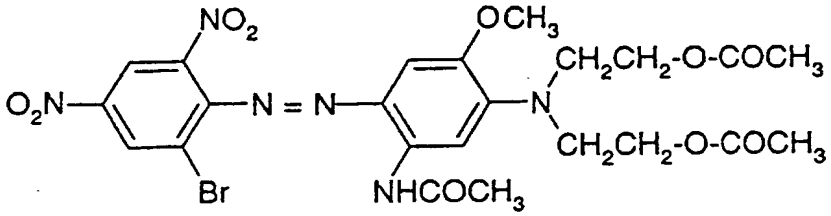

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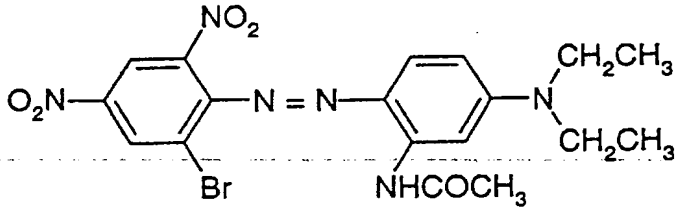

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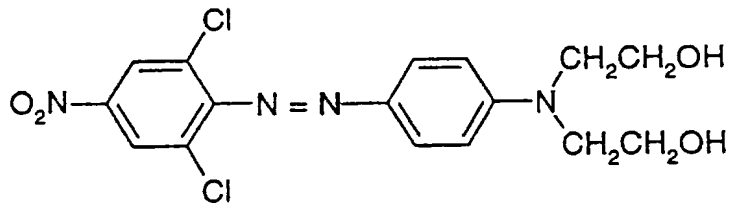
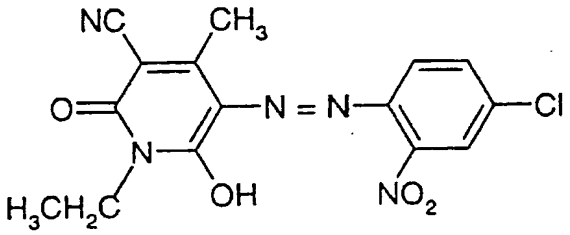


(37).

13. A dye mixture according to either claim 1 or claim 2, which comprises the dyes of formulae



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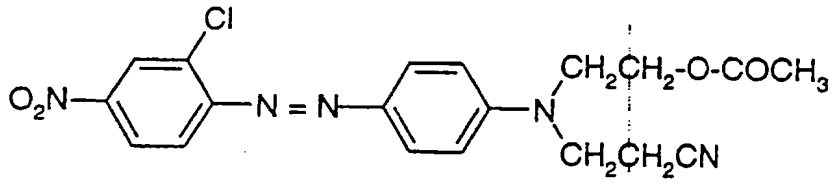

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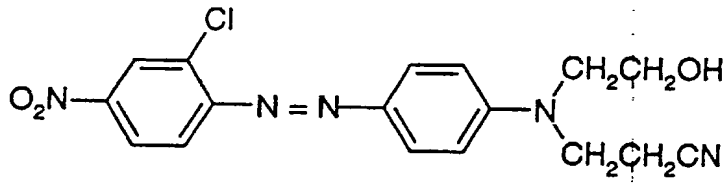

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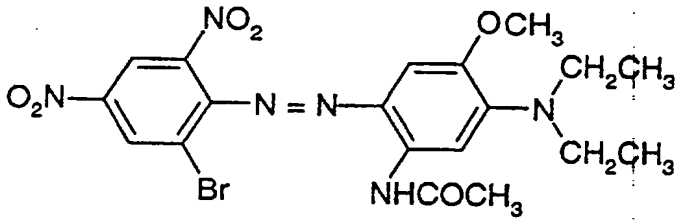

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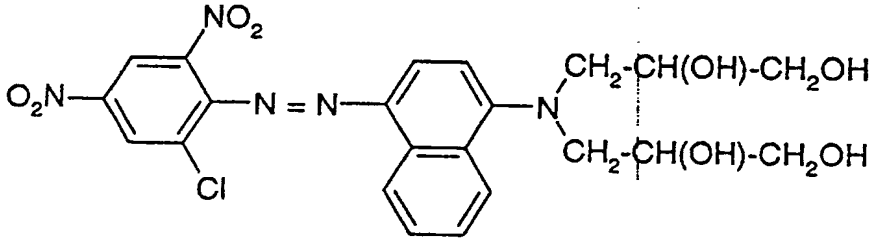

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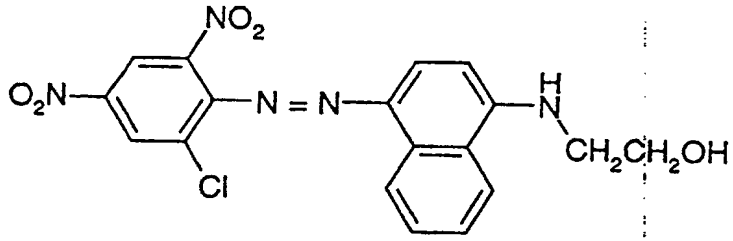

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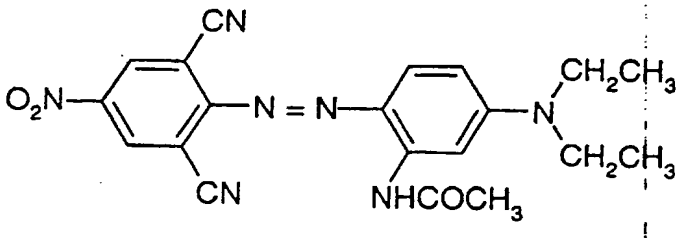

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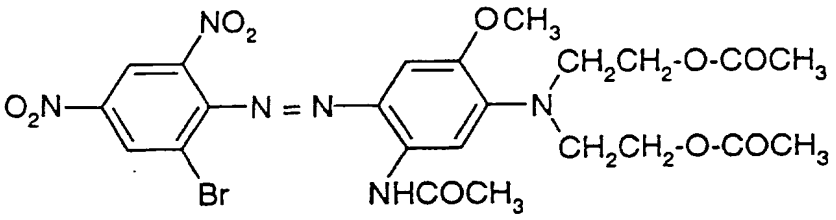

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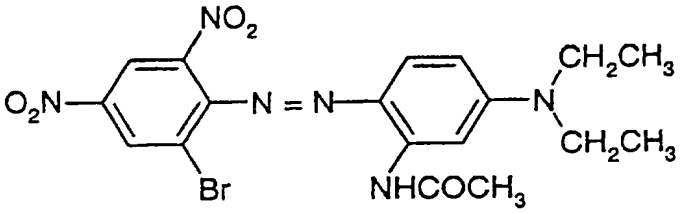

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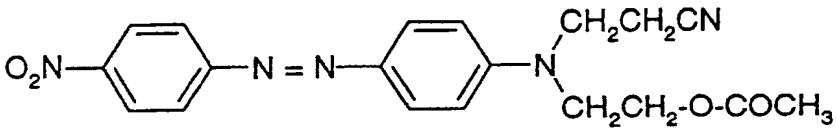

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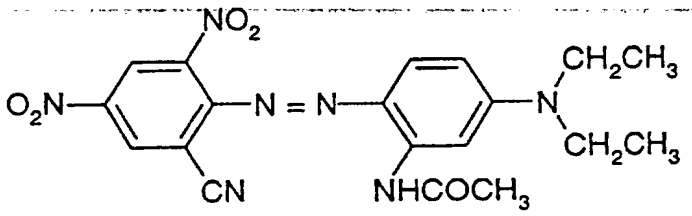

(38).

14. Use of the dye mixture according to either claim 1 or claim 2 for dyeing or printing cellulose acetate-containing fibre materials.

15. A process for dyeing or printing cellulose acetate-containing fibre materials, wherein a dye mixture according to either claim 1 or claim 2 is applied to, or incorporated into, these materials.

16. A process according to claim 15, wherein the cellulose acetate-containing fibre material is cellulose-2$^1/_2$acetate or cellulose triacetate.

17. The fibre material dyed by the process according to either claim 14 or claim 15.

The Patent Office

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Application No: GB 0001184.1
Claims searched: 1-17

Examiner: Stephen Quick
Date of search: 22 March 2000

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R):

Int Cl (Ed.7): C09B 67/22

Other:

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	EP 0827988 A1	(DYSTAR TEXTILFARBEN), see especially examples 1 & 2, and page 8, line 40	1 at least
X	EP 0802239 A1	(NIPPON KAYAKU), see especially examples 1-3, 6 & 7, comparative examples 1 & 3-5, and page 7, lines 3-4	1 at least
X	EP 0735110 A1	(DYSTAR JAPAN), see especially examples 2 & 3, and page 8, line 33	1 at least
X	EP 0684290 A2	(HOECHST MITSUBISHI KASEI), see especially examples 6, 7-1, 7-2 & 7-6	1 at least
X	WO 97/21773 A1	(BASF), see especially examples 1-6 & 8, and abstract, last two lines	1 at least
X	WO 97/21772 A1	(BASF), see especially examples 4, 6-8 & 10, and abstract, penultimate line	1 at least
X	WO 96/16129 A1	(BASF), see especially examples 3 & 4, and page 10, line 2	1 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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